

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

NO DRAWINGS

Improvements in or relating to Vinylation of Tertiary Alcohols

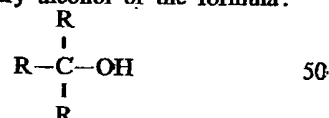
We, HERCULES POWDER COMPANY, a corporation organized under the laws of the State of Delaware, one of the United States of America, of 900 Market Street, City of Wilmington, Zone 99, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the preparation of vinyl ethers of tertiary alcohols by the direct reaction of acetylene and a tertiary alcohol.

It is known that primary and secondary alcohols can be vinyated readily by reacting the alcohol in the liquid phase with acetylene in the presence of an alkali metal alkoxide catalyst. Tertiary alcohols, however, are not so readily vinyated; it is reported in the literature, for instance, that tertiary alcohols can be vinyated only incompletely and that the degree of vinylation possible is dependent on the equilibrium characteristics of the particular tertiary alcohol sought to be vinyated. It is significant, for instance, that when tertiary alcohols can be vinyated only incompletely and that the degree of vinylation possible is dependent on the equilibrium characteristics of the particular tertiary alcohol sought to be vinyated. It is significant, for instance, that when tertiary butyl alcohol is subjected to 200 p.s.i.g. acetylene pressure for 8 hours at 180°C. in the presence of potassium tertiary butoxide, the yield of tertiary butyl vinyl ether is considerably less than 10%. Higher conversions may be realized by using larger amounts of alkoxide catalyst but this approach is not practical because of increased costs, gelling of the reactants, and explosion hazards.

[Price 4s. 6d.]

According to the present invention, there is provided a process for preparing vinyl ethers of tertiary alcohol which comprises reacting a tertiary alcohol of the formula:



wherein each R (which may be the same or different) is an alkyl, aryl, aralkyl, alkaryl or cycloalkyl radical and wherein 2 Rs may, together with the carbon atom attached to the hydroxyl group, be a cycloalkyl radical, in the liquid phase with acetylene at a temperature of from 100°C. to 250°C. and at an elevated pressure of up to 500 p.s.i.g. in the presence of a catalyst comprising an alkali metal alkoxide and an oxide of an alkaline earth metal or of magnesium.

The invention is illustrated by the following examples in which parts and percentages are by weight unless otherwise specified.

Example 1

Into a reaction vessel equipped with a water-cooled reflux condenser and mechanical stirred there were placed 56 parts of potassium and 1170 parts of tertiary butyl alcohol. The contents of the reactor were then heated to reflux temperature under a nitrogen atmosphere until the potassium had reacted with the alcohol. The resultant solution of potassium tertiary butoxide was then charged into a stainless steel autoclave equipped with a mechanical stirred along with 100 parts of powdered calcium oxide. The autoclave was flushed and tested with nitrogen and the reactants were then heated while agitating to 130°C. At this point the autoclave was pressured to 145 p.s.i.g. with acetylene and for the next 9-3/4 hours the reaction was continued while maintaining a temperature of 130-165°C. and an acetylene

Price 25p

pressure of 130-195 p.s.i.g. At this point the absorption of acetylene had ceased. The autoclave was then cooled and flushed with nitrogen after which it was opened and the product discharged. The product amounted to 1182 parts and by near infrared analysis was found to comprise more than 90% tertiary butyl vinyl ether.

Example 2

This example was carried out in the same manner as Example 1 with the exception that 100 parts of magnesium oxide was used in place of calcium oxide. The temperature range was 130-150°C., the acetylene pressure 80-130 p.s.i.g. and the reaction time 12 hours. The product amounting to 1361 parts was found by near infrared analysis to contain 30% tertiary butyl vinyl ether.

Example 3

The general procedure of this example also was the same as in Example 1. Initially, 7.5 parts potassium and 156 parts of tertiary butyl alcohol were reacted to form a solution of potassium tertiary butoxide in excess alcohol. The resulting solution was charged along with 14 parts of powdered calcium oxide into the autoclave and reaction conditions of 130-180°C. and 160-240 p.s.i.g. acetylene pressure were maintained for 10 hours. The product amounting to 166 parts was found to contain 95% tertiary butyl vinyl ether by near infrared analysis.

Example 4

Following the general procedure of Example 1, 5.6 parts of potassium and 118 parts of tertiary butyl alcohol were reacted to form a solution of potassium tertiary butoxide in excess alcohol. The resulting solution was charged along with 0.5 part of barium oxide into the autoclave and reaction conditions of 150°C. and 120-150 p.s.i.g. acetylene pressure were maintained for 1-3/4 hours. The product amounting to 129 parts contained 26.7% tertiary butyl vinyl ether.

Example 5

Following the general procedure of Example 1, 430 parts of α,α -dimethylbenzyl alcohol and 17.6 parts of potassium were reacted to form a potassium alcoholate solution which was vinylated in the presence of 22.4 parts of powdered calcium oxide at 128-130°C. and 120-240 p.s.i.g. acetylene pressure for 12 hours. There was obtained 523.5 parts of product which contained 80.4% vinyl ether of α,α -dimethylbenzyl alcohol.

Using the same technique in the absence of calcium oxide the product contained only 8.4% of the vinyl ether.

The process of the invention is applicable to any tertiary alcohol of the formula given above. Typical alcohols that can be used in the process of the invention include triphenyl methanol, 1,1-dimethyl-n-butanol, 1,1-dimethyl (p-methylbenzyl) alcohol, 1-methylcyclohexanol, dihydro- α -terpineol

and 1,1,2,2-tetramethyl propanol.

As stated above, the temperatures in the process of the invention should be from 100°C. to 250°C. At temperatures below 100°C. the rate of reaction is too low for practical purposes, while the upper temperature limit which should be used is also governed by practical considerations, being limited to the temperature at which thermal decomposition of the product occurs and by the safety consideration involved in the handling of acetylene under pressure. In most cases it is not necessary to exceed a temperature of 200°C. The acetylene pressure also is widely variable within the above defined range. While the rate of vinylation is proportional to pressure, the reaction nevertheless proceeds readily at relatively low pressures and a pressure from atmospheric pressure upward can be satisfactory, the upper limit on the pressure being dictated by safety and practicability. Temperature and pressure are, of course, controlled interrelatedly to maintain the reactant alcohol in the liquid phase.

As is evident from the examples this reaction can be carried out without the addition of an inert solvent or diluent. The process, however, is operative in the presence of inert solvents and diluents, and these can be employed for convenience if so desired. Typical diluents include benzene, toluene and similar inert hydrocarbons.

In the examples, a potassium alkoxide of the alcohol undergoing vinylation was employed as catalyst as a matter of convenience. However, the alkoxide may be that of any alkonal, primary, secondary or tertiary, and may be that of any alkali metal, e.g., sodium, lithium, rubidium, etc., as well as potassium. In short any alkali metal alkoxide as used in the prior art is satisfactory although it is preferred to employ an alkoxide of the alcohol to be vinylated. The amount of alkoxide is also consistent with the amounts utilized in the prior art and will typically be from about 0.1 to 10% by weight of the alcohol reactant.

The function of the metal oxide in the process is not fully understood but appears to be that of a promoter for the catalyst. In any event, it does not appear to function as a dehydrating agent because other materials capable of absorbing water, e.g., alumina, have no effect on the reaction when employed in place of the metal oxide.

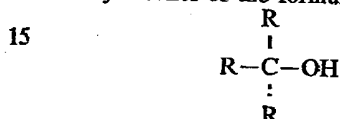
Regardless, however, of how the metal oxide functions in the process, it too can be widely varied in amount. In general, an amount ranging from about 0.1 to 10% by weight of the alcohol reactant will have a beneficial effect but from the standpoint of convenience and for economic reasons it is recommended that the amount be within the range of 0.1 to 1% by weight of the alcohol. Although oxides of magnesium, calcium,

barium, and strontium can be used in the process, that of calcium is preferred as having the most pronounced beneficial effect.

We are aware of the Home Office regulations regarding acetylene, e.g. the Compressed Acetylene Order, 1947, S.R. and O. 1947, No. 805, and we make no claim to the use of the present process in contravention of these regulations.

10 WHAT WE CLAIM IS:—

1. A process of preparing vinyl ethers of tertiary alcohols which comprises reacting a tertiary alcohol of the formula:



20 wherein R is an alkyl, aryl, aralkyl, alkaryl or cycloalkyl radical and wherein two Rs may, together with the carbon atom carrying the hydroxyl group, form a cycloalkyl radical, in the liquid phase with acetylene at a temperature of from 100°C. to 250°C. and

at an elevated pressure of up to 500 p.s.i.g. 25 in the presence of a catalyst comprising an alkali metal alkoxide and an oxide of an alkaline earth metal or of magnesium.

2. A process according to Claim 1 in which the alcohol is tertiary butyl alcohol. 35

3. A process according to Claim 1 or 2 in which the alkoxide is the potassium alkoxide of the alcohol reactant.

4. A process according to Claim 1, 2 or 3 in which the metal oxide is calcium oxide. 40

5. A process according to Claim 1 for preparing vinyl ethers of tertiary alcohols, substantially as hereindisclosed with particular reference to the Examples.

6. Vinyl ethers of tertiary alcohols whenever prepared in accordance with any one of Claims 1 to 5.

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